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Effect of alloying on the kinetics of CO + O_2 and CO + NO reactions on Pt-Rh nanocatalysts : a theoretical model

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Abstract : Surface Chemistry Reaction Model has been used to study the kinetics of CO + NO and CO + O_2 reactions on Pt-Rh nanocatalysts. For CO + O_2 reaction the alloy particles evince an intermediate behaviour; however, for the CO + NO reaction the alloy particles show no synergistic effect of alloying The inherent rate of CO + O_2 reaction is much higher than that of CO + NO reaction on the $Pt_{50}Rh_{50}$ nanoparticles. The kinetics of the CO + NO + O_2 and CO + NO reaction on the alloy particles are almost the same NO inhibits formation of CO_2 molecules. The simulated results are in qualitative agreement with the experimental findings

Keywords : Surface Chemistry Reaction Model, nanocatalysts, Monte Carlo simulation.

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1. Introduction

Because of the ever-increasing road traffic there has been a stringent, on-going demand for low auto emissions. CO oxidation and NO reduction are the two most important reactions in controlling pollution from automobile exhaust gases. The ceria-supported Pt-Rh bimetallic catalysts are known to be the most effective three-way catalysts for simultaneous elimination of the CO, NO and uncombusted hydrocarbons from automobile exhaust gases [1]. These catalysts are being increasingly used globally in the catalytic converters of automobiles. Therefore, it is important to study the surface composition and catalytic activity of these bimetallic nanocatalysts under different working conditions of the catalytic converter. Surface composition plays a vital role in catalysis by virtue of the interaction between the surface atoms and the adsorbed atoms and molecules. The surface atoms are often exposed to absorbates at different times in the catalytic converter. Among the important reactants in the catalytic converter CO, NO and O_2 deserve special mention. In our earlier works, we have studied the surface composition and segregation of the Pt-Rh nanoparticles under a host of conditions [10-12]. In this paper, we present the result of our theoretical investigations on the kinetics of CO + NO and CO + O_2 reactions on the Pt-Rh bimetallic particles. These two reactions are most extensively studied reactions because of their relevance to the environmental pollution control. We have studied the effect of alloying on the kinetics of these two essential reactions in the catalytic converters. The plan of the paper is as follows : In section 2, the theoretical model used in the present work is briefly outlined. The results are presented in section 3. The conclusions are drawn in section 4.

2. Theoretical Model

We take recourse to the Surface Chemistry Reaction Model [2,3] in order to study the kinetics of CO + O_2 and CO + NO reactions on Pt, Rh and the $Pt_{50}Rh_{50}$ nanoparticles.

A. Kinetics of CO oxidation (CO + O_2 reaction) :

For the CO + O_2 reaction the following elementary stepes were considered [2,3]-(i) Adsorption of CO molecules onto the surface of the metal or the alloy, (ii) desorption of CO molecules from the surface of metal/alloy, (iii) adsorption of O_2 molecules on the surface followed by adsorption of

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atomic oxygen and (iv) formation of CO_2 molecules through the combination of adsorbed CO molecule and oxygen atom.

$$CO \Leftrightarrow CO_a \quad (1)$$

$$O_2 \rightarrow 2O_a \quad (2)$$

$$CO_a + O_a \rightarrow CO_2 \quad (3)$$

The suffix 'a' denotes the component in the adsorbed phase.

Table 1. Parameter values used in model calculations for CO + O_2 Reaction [2,3].

	Pt	Rh
CO adsorption		
σ (cm²/mole)	3.65 x 10^8	3.75 x 10^8
S_{CO}	0.5	0.5
CO desorption		
A (s^{-1})	1.0 x 10^{13}	1.6 x 10^{14}
E (kcal/mole)	29.63	31.6
α_{co} (kcal/mole)	6.5	4.5
O_2 adsorption		
S_o	0.012	0.01
CO_2 formation		
A (s^{-1})	1.0 x 10^{13}	1.0 x 10^{12}
E (kcal/mole)	13.5	14.3

The rate of adsorption of species i on metal m is given by molecular collision theory [2,3,7] : $(r_{a,i})_m = (RT/2\pi M_i)^{1/2} \sigma_m (S_i)_m C_i \theta_v$, where M_i is the molecular weight of the species i; σ_m is the the area occupied by 1 mole of surface atoms (cm²/mole) of the metal m; $(S_i)_m$ is the initial sticking coefficient of the species i on the metal m. C_i is the concentration of the component i in the gap phase and is calculated from the gas pressure through the relation $C_i = \frac{P_i}{RT}$ (moles/c.c.). θ_v is the fraction of vacant surface sites available for adsorption, R the universal gas constant and T is the temperature (in Kelvin).

The rate of desorption of CO [2,3] is given by $r_{d,CO} = A.\exp-\{(E-\alpha_{CO}\theta_{CO})/RT\}\theta_{CO}$, where A is the pre-exponential factor (s^{-1}); E, the activation barrier (kcals/mole) for CO desorption: α_{CO}, the interaction parameter (kcals/mole) and θ_{CO}, the surface coverage of CO. The rate of formation of CO_2 molecules is given by [2,3] $r_{CO_2} = A.\exp(-E/RT).\theta_{CO}.\theta_O$, where θ_O is the surface coverage of adsorbed oxygen atom. In the expression for r_{CO_2}, A and E denote the preexponential factor and activation barrier for CO_2 formation

The steady state continuity equations for the adsorbed surface species CO_a and O_a are given by [2,3] :

$$r_{a,CO} - r_{d,CO} - r_{CO_2} = 0 \quad (4)$$

$$2r_{a,O_2} - r_{CO_2} = 0 \quad (5)$$

Now, for the purpose of studying the kinetics of the CO + O_2 reaction, one has to solve the equations (4) and (5) self-consistently for θ_{CO} and θ_O.

Approximation for the alloy :

With a view to studying the kinetics of CO + O_2 and CO + NO reaction on the surface of the $Pt_{50}Rh_{50}$ alloy particles, we resort to the first order approximation as it is the simplest approximation.

The rate of adsorption of CO on Pt [2] and Rh [3] are respectively given by $(r_{a,CO})_{Pt} = (RT/2\pi M_{CO})^{1/2} \sigma_{Pt} S_{CO} C_{CO} \theta_v$ and $(r_{a,CO})_{Rh} = (RT/2\pi M_{CO})^{1/2} \sigma_{Rh} S_{CO} C_{CO} \theta_v$, where $\theta_v = 1 - \theta_{CO}$ [3]. In our studies on the alloy particles, the rate of adsorption has been taken to be a linear combination of these two *i.e.* $(r_{a,CO})_{alloy} = (x_s)_{Pt}(r_{a,CO})_{Pt} + [1-(x_s)_{Pt}] (r_{a,CO})_{Rh}$. Here, $(x_s)_{Pt}$ is the surface concentration of Pt atoms on the surface of the supported Pt-Rh nanoparticles.

The other elementary reaction steps were also treated on the same footing. The values of the surface concentration of Pt atoms, $(x_s)_{Pt}$ were taken from our earlier Monte Carlo calculations [12].

B. Kinetics of CO + NO reaction :

For the CO + NO reaction the following elementary steps were considered [3-5]: (i) adsorption and desorption of CO and NO, (ii) dissociation of molecularly adsorbed NO into adsorbed atomic nitrogen and oxygen atom, (iii) formation of N_2 molecules through two possible steps, namely, β-N_2 and δ-N_2 steps and finally, (iv) formation of CO_2 molecules through the combination of adsorbed CO and O.

$$CO \Leftrightarrow CO_a \quad (6)$$

$$NO \Leftrightarrow NO_a \quad (7)$$

$$NO_a \rightarrow N_a + O_a \quad (8)$$

$$N_a + N_a \rightarrow N_2 \ (\beta\text{-}N_2) \quad (9)$$

$$NO_a + N_a \quad N_2\ (\delta\text{-}N_2) + O_a \tag{10}$$

$$CO_a + O_a \rightarrow CO_2 \tag{11}$$

The rate of adsorption of NO [3] is given by $r_{a,NO} = (RT/2\pi M_{NO})^{1/2}\sigma_m S_{NO} C_{NO}\theta_v$. However, here $\theta_v = 1 - \theta_{CO} - \theta_{NO} - \theta_N$ [3]. For the CO + NO reaction, the rate of

Table 2. Parameter values used in model calculations for CO + NO reaction [2-6].

	Pt	Rh
CO adsorption		
S_{CO}	0.5	0.5
CO desorption		
$A(s^{-1})$	1.0×10^{13}	1.6×10^{14}
E (kcal/mole)	29.63	31.6
α_{CO} (kcal/mole)	6.5	4.5
α_N (kcal/mole)	0	10
CO_2 formation		
A (s^{-1})	1.0×10^{13}	1.0×10^{12}
E (kcal/mole)	13.5	14.3
NO adsorption		
S_{NO}	0.5	0.5
NO desorption		
A (s^{-1})	5×10^{13}	5×10^{13}
E (kcal/mole)	26	26
NO dissociation		
A (s^{-1})	3.0×10^{10}	3.0×10^{10}
E (kcal/mole)	29	19
δ-N_2 formation		
A (s^{-1})	-	2×10^{9}
E (kcal/mole)	-	21
β-N_2 formation		
A (s^{-1})	1.3×10^{11}	3.0×10^{10}
E (kcal/mole)	20.2	31
α_N (kcal/mole)	0	4

desorption of CO [3] is given by $r_{d,CO} = A.\exp - \{(E - \alpha_{CO}\theta_{CO} - \alpha_N\theta_N)/RT\}.\theta_{CO}$; the rate of NO dissociation is given by $r_{diss,NO} = A.\exp\left(-\frac{E}{RT}\right).\theta_{NO}.\theta_V$ and the rates of N_2 formation [3] are given by $r_{N_2,\delta} = A.\exp\left(-\frac{E}{RT}\right)\theta_{NO}.\theta_N$ and $r_{N_2,\beta} = A \exp - \{(E - \alpha_N\theta_N)/RT\}\theta_N^2$. Here also we have used the same approximation for the alloy. δ-N_2 formation step is not found to occur on Pt [4,5].

The steady state continuity equations for the adsorbed species CO_a, No_a, N_a and O_a are given by [3,7] :

$$r_{a,CO} - r_{d,CO} - r_{CO_2} = 0 \tag{12}$$

$$r_{a,NO} - r_{d,NO} - r_{diss,NO_2} - r_{N_2\delta} = 0 \tag{13}$$

$$r_{diss,NO} - r_{N_2\delta} - 2r_{N_2,\beta} = 0 \tag{14}$$

$$r_{diss,NO} + r_{N_2\delta} - r_{CO_2} = 0 \tag{15}$$

Table 3. MC-simulated surface concentration of Pt, (x_s)Pt at different temperatures T (in Kelvin) [12].

T (in Kelvin)	(x_s)Pt
450	0.548
475	0.551
500	0.559
525	0.553
550	0.538
575	0.564
600	0.528
625	0.554
650	0.572
675	0.523

For studying the kinetics of the CO + NO reaction, one has to solve the set of above four equations self-consistently for θ_{CO}, θ_{NO}, θ_N and θ_O. Finally, we arrive at r_{CO_2} as it is an important yardstick for comparing the rates of different reactions, namely, CO + O_2, CO + NO and CO + NO + O_2. For the purpose of studying the kinetics of the CO + NO + O_2 reaction one merely requires to add the term $2r_{a,O_2}$ to the left hand side of equation 15. We make use of the same alloy approximation for studying the kinetics of CO + NO + O_2 reaction on the $Pt_{50}Rh_{50}$ alloy particles.

3. Results and discussions

The rate constants used in our studies are tabulated in Tables 1 and 2 (with references). The Monte Carlo simulated $(x_s)_{Pt}$ *vs.* T results used in the work are given in Table 3.

A comparative study of the kinetics of the CO + O_2 reaction on three different systems is depicted in Figure 1. The turnover number is nothing but the number of CO_2 molecules that are released per site per second. The rate of formation of CO_2 molecules is found to be higher on Pt than on Rh which is quite obvious. It is quite evident from the rate constants (*i.e.* pre-exponential factor and activation barrier) and the expression for the rate of formation of CO_2 molecules (r_{CO_2}) in Table 1 that Pt is a better catalyst for CO oxidation (or CO + O_2 reaction). The $Pt_{50}Rh_{50}$ alloy particles show an intermediate behaviour.

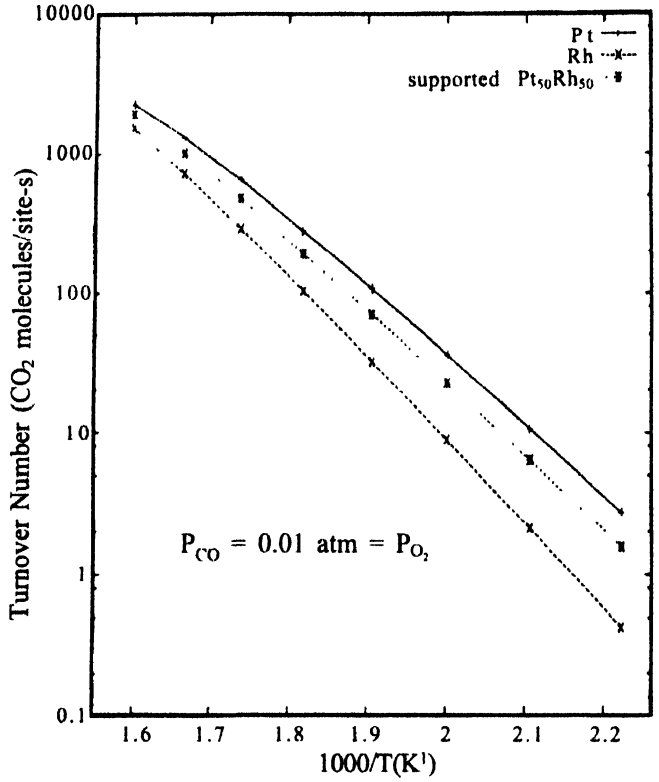

Figure 1. A comparison of the specific rates of CO oxidation (*i.e.* CO + O_2 reaction) on three different systems at partial pressure of CO, P_{CO} = 0.01 atm = partial pressure of O_2, P_{O_2}.

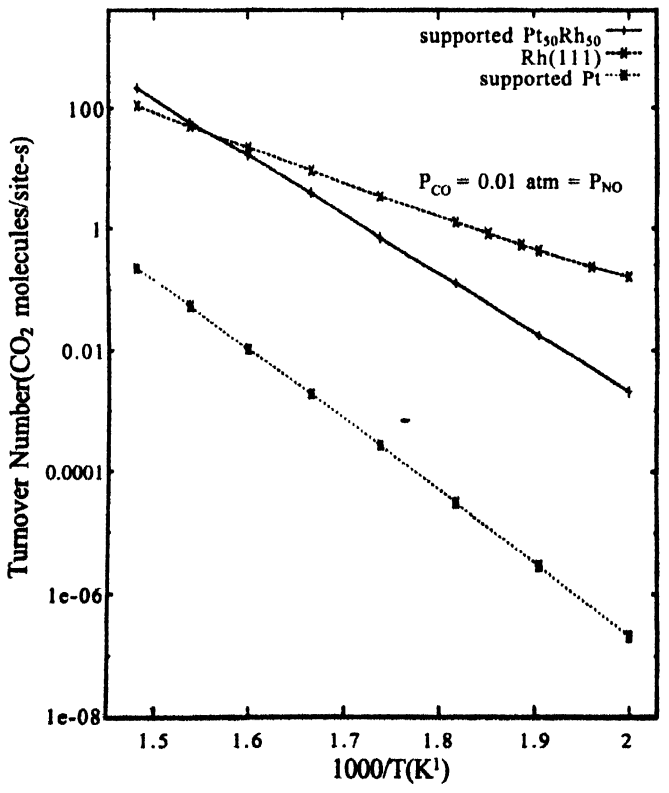

Figure 2. A comparative study of the rate of CO + NO reaction on three different systems at parital pressure of CO, P_{CO} = partial pressure of NO, P_{NO} = 0.01.

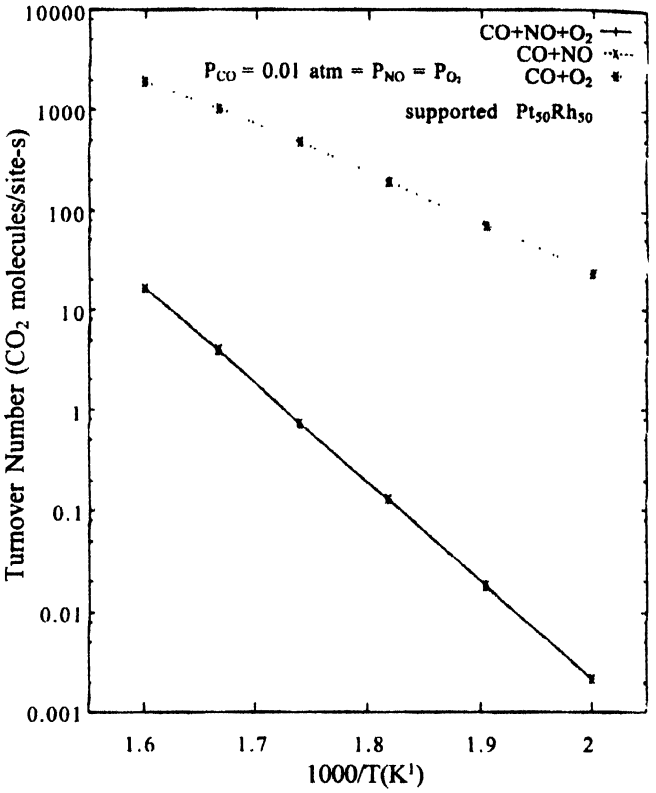

Figure 3. A comparative study of the specific rates of three different reactions on the supported $Pt_{50}Rh_{50}$ nanoparticles at partial pressure of CO, P_{CO} = partial pressure of NO, P_{NO} = partial pressure of O_2, P_{O_2} = 0.01.

Figure 2 compares the rate of the CO + NO reaction on three different systems. It may be noticed that the turnover number for the formation of CO_2 molecules is considerably higher on Rh and the alloy particles closely resemble the kinetic behaviour of Rh. The low turnover number for formation of CO_2 molecules on supported Pt can be attributed to its low NO dissociation capability. The NO dissociation step is the most important step in CO + NO reaction because it furnishes the adsorbed oxygen atom with which molecularly absorbed CO can unite to form CO_2 molecule. That is to say, for the CO + NO reaction the rate of formation of CO_2 molecules is controlled by the rate of NO dissociation. The activation barrier for NO dissociation is much higher on Pt. In other words, the rate of NO dissociation on Pt is very small. Thus, the rate of formation of CO_2 molecules suffers a sharp decline on Pt. Now, Pt is a good catalyst for CO oxidation and Rh for No reduction; however, the alloy particles show no synergistic effect of alloying. This observation is corroborated by experimental findings [8].

In Figure 3 it may be observed that the inherent rate

of CO + O_2 reaction is much higher than that of CO + NO reaction on the supported alloy particles. It is also evident that the kinetics of CO + NO and CO + NO + O_2 reaction on the supported alloy particles are almost the same as their plots fall upon each other. From this observation one can at once infer that the presence of NO in the gas mixture inhibits the formation of CO_2. This finding is in agreement with the experimental results [9].

4. Conclusion

Surface Chemistry Reaction Model has been used to study the effect of alloying on the kinetics of CO + O_2 and CO + NO reaction on the $Pt_{50}Rh_{50}$ nanocatalysts. The alloy particles show no synergistic effect of alloying. The pressence of NO in the gas mixture inhibits the formation of CO_2 molecules. Though the model is very simple, it can account for many experimentally observed facts. We believe that the present findings can be gainfully exploited in three-way catalysis.

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